Molecular Dynamics in Strong Laser Fields

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(Invited Paper)

***Abstract*—One of the goals for strong field physics is imaging the dynamics of the quantum systems, and in case of molecules, there is strong interest in imaging of the electron rearrangement during chemical reactions. Strong field ionization of molecules has many attractive features that make this process a candidate tool for strong field imaging of transient states and chemical reactions. In this paper, we present analysis of ionization dependence on orientation of molecular axis with respect to polarization of the electric field of the laser. By considering several examples of molecules at their equilibrium internuclear distances and an example of the simplest chemical reaction, namely, the dissociation of diatomic molecule, we present how symmetries of the molecular orbitals influence the alignment-dependent ionization and how this dependence can be used to follow molecular dynamics using strong field multiphoton ionization.**

***Index Terms*—Diatomic molecules, ionization, multiphoton processes.**

I. INTRODUCTION

IN THE last two decades, laser technology has experienced huge evolution in the intensity, frequency, and time domain. Under these conditions new, highly nonlinear laser-induced phenomena were discovered such as above-threshold ionization (ATI), high-order harmonic generation, as well as modifications of some well-known processes by the presence of an intense laser pulse were observed. While the dynamical aspects of ionization of atoms in a strong laser field are considered to be well-understood nowadays, theoretical analysis of the same process in more complex targets, such as diatomic and polyatomic molecules, is a topic of active research. Recent experiments showed that the behavior of molecules in such intense laser fields is essentially different from weak field conditions. There have been observed new phenomena, such as Coulomb explosion, bond softening, vibrational trapping, optically triggered explosions, and above-threshold dissociation. Already the simplest process possible, namely, multiphoton sequential ionization, has revealed many new features in comparison to atoms. Among the various processes induced by an intense laser field, it is of fundamental importance to understand the ionization mechanism and its properties since most measurements and manipulations of molecules are achieved for ionized systems. Moreover, ionization is a process that is followed by various interesting secondary processes such as fragmentation or processes induced, e.g., by the rescattering of the photoelectron. Ionization is also an interesting physical process in itself, showing a crossover of the mechanism from perturbative multiphoton absorption to nonperturbative multiphoton ionization to tunnel and field ionization. Finally, molecular ionization may provide insights into methods of molecular imaging since Corkum and coworkers [1] have shown that another strong field process, namely, high harmonic generation may be exploited to tomographically image the highest occupied molecular orbital (HOMO) for diatomic molecules. Intrinsic features of the molecule such as its geometry and the symmetry of the electronic wave function influence the photoionization cross section that leads to the possibility of an inversion of the problem, namely, on gaining detailed information on the molecular structure by studying (multi) photoionization observables.

So far, ionization of two- and three-atomic molecules have especially been studied in great detail. For example, for molecules like N_2, O_2 [2]–[5], HCl [6], CS_2 [7]–[9], and CO_2 [10] not only ionization yields were measured and fragmentation was observed, but also photoelectron angular distributions were determined. Furthermore, strong field ionization of a series of organic molecules [11], [12], methyl iodide [13], unsaturated linear hydrocarbons [14], and different chlorinated and fluorinated benzene derivatives [15], [16] as well as amines [17], alkanes [18], alcohols [19], oxylene [20], and cyclopentanone [21] have been studied. Among other results, it has been found, by measuring the ionization yields, that such complex molecules are generally harder to ionize than the atoms with comparable ionization potentials. Moreover, due to new developments in molecular alignment technique, a lot of research has been devoted to the study of ionization for aligned molecules. For example, angle-dependent ionization signal has been studied in [22]. Additionally, angular electron distributions look differently for different degrees of alignment [23].

Some of the most recent theoretical developments in strong laser physics are quantum dynamical versions of the configuration interaction (CI) and multiconfiguration self-consistent field methods of electronic structure calculations. These interesting approaches, time-dependent CI with single excitations [24], [25] and time-dependent Hartree–Fock [26] as well as multiconfiguration time-dependent Hartree–Fock [27]–[29], can treat the correlated motion of many electrons in nonequilibrium situations. However, so far, they were applied to small or artificial model molecules. An exception is time-dependent density-functional theory [30]–[35] that, in principle, has a potential to describe strong field processes for di- and polyatomic molecules. Much progress has been made in the development of *ab initio* time-dependent theoretical simulations by direct solution of the Schrödinger equation of the system of interest. Since such

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calculations require a large space–time grid, and hence, an enormous computational power, current investigations are limited to one- and two-electron molecules, e.g., H_2^+ and H_2 for recent papers see [36]–[40].

In this paper, we will use an alternative approach to study the ionization of diatomic molecules in strong laser fields, namely, the so-called intense-field many-body S-matrix theory (IMST) or strong field approximation (SFA). This theoretical approach accounts nonperturbatively for the intense-field interaction already in the lowest order of the S-matrix expansion. Moreover, the first-order term takes direct account of the structural symmetry of the molecular orbital from which the electron is ionized by the laser field. Details of the S-matrix approach will be presented in the next section. In Section III, we will show how the different structural symmetries of a diatomic molecule (namely, σ- versus π-symmetry and gerade versus ungerade symmetry) are reflected in the total ionization rates of the molecule as a function of the alignment angle between the polarization direction of a linearly polarized laser field and the internuclear axis of the molecule. To this end, we will first consider the basic examples of ionization from the energetically well-separated valence orbitals N_2, O_2, and C_2 at equilibrium distance. Finally, we consider a dynamic case in Section IV and present alignment-dependent ionization rates of the excited Br_2 molecule at different internuclear distances (reflecting the dissociation of the molecule) and discuss how the results can provide insights in the electron rearrangement in the valence shells of the dissociating molecule. The paper ends with a summary.

II. THEORY

IMST provides a systematic approximation method for intense-field problems. The earliest forms of S-matrix theories that accounted nonperturbatively for the intense-field interaction are typified by the well-known Keldysh–Faisal–Reiss (KFR) model or SFA [41]–[43], where the interaction with the laser field is emphasized. IMST has been developed [44] as an extension of this model and provides systematic expansion schemes. The IMST has been extended to investigate multiphoton ionization from the outer and inner valence shells of a diatomic and polyatomic molecules [22], [23], [44]–[46] as well as fullerenes [47], [48].

Recent investigations on multiphoton ionization of diatomic molecules, carbon clusters [22], [50], hydrocarbons [51], and fullerenes [47], [48] helped to explain the phenomenon of suppressed ionization of molecules observed experimentally. It was shown that this phenomenon occurs due to effective destructive interference between the subwaves of the ionizing electrons emerging from different atomic centers. For example, the antibonding symmetry of the HOMO in O_2 gives rise to a destructive interference between the two subwaves, which leads to a suppression of the low-energy part of the ATI spectrum, and consequently, of the total ion yields. For a molecule with many atoms, such as C_{60}, this extends to a molecular multislit-like interference effect among the electron waves emanating from the many nuclear centers of a molecule that can drastically reduce the ionization probability as compared to an atom having the same ionization potential. Excellent agreement has been found between the results obtained within the S-matrix theory and the experimental data for the saturation intensities of the different charge states of C_{60} for ultrashort laser pulses [47]. Moreover, systematic study of ATI of carbon clusters within the lowest order of the intense-field many-body S-matrix expansion revealed several interesting phenomena, such as symmetry-dependent modulation of the contributions of partial yields for electron emission from several inner valence orbitals to the total ionization yields, dependence of the photoelectron angular distributions on the orbital symmetry, as well as characteristic minima in the high-energy photoelectron spectra whose positions depend on the detailed properties of the molecular orbital.

Here, we analyze some characteristics of alignment-dependent ionization for diatomic molecules with orbitals of different symmetries, using the leading order term of the S-matrix expansion. It involves a transition matrix element between the initial-state wave function of a bound state of the molecule, $|\Phi_i\rangle$, and the product state of the Volkov wave function of the emitted electron in the field, $|\xi_{\mathbf{k}_N}\rangle$, and the unperturbed final bound-state wave function of the residual molecular ion, $|\Phi_f^+\rangle$, and is corrected approximately for the long-ranged Coulomb interaction in the final state. The total ionization rate from an active orbital with N_e equivalent electrons in a linearly polarized laser field is given by (Hartree atomic units, $e = m_e = \hbar = 1$, are used)

$$\begin{aligned}\frac{dW_{fi}^{(N)}(I,\hat{\mathbf{n}})}{d\Omega} &= 2\pi\, N_e\, C_{\mathrm{coul}} \sum_{N=N_0}^{\infty} k_N\, (U_p - N\omega)^2 \\ &\quad \times \int d\hat{\mathbf{k}}_N\, J_N^2\left(\alpha_0 \times \mathbf{k}_N, \frac{U_p}{2\omega}\right) \\ &\quad \times |<\xi_{\mathbf{k}_N}\, \Phi_f^+ |\Phi_i > (\hat{\mathbf{n}})|^2 \qquad (1)\end{aligned}$$

where $C_{\mathrm{coul}} = ((2I_p)^{3/2}/E_0)^{2Z/\sqrt{2I_p}}$ is a Coulomb factor accounting for the interaction of the emitted electron with the residual ion of charge state $Z = 1$. E_0 is the peak field strength of the laser and I_p is the ionization energy of the molecule. $J_N(a;b)$ is a generalized Bessel function of two arguments, where $\alpha_0 = \sqrt{I}/\omega$ is the quiver radius and $U_p = I/4\omega^2$ is the quiver energy of an electron in a laser field of frequency ω and intensity I. $k_N^2/2 = N\omega - U_p - I_p$ is the kinetic energy of an electron on absorption of N photons from the field. N_0 is the minimum number of photons to be absorbed to ionize the molecule. In this paper, we concentrate on rates for ionization and assume that the electric field of a laser can be described as a monochromatic wave. In order to include the effects of finite laser pulse and both temporal and spatial characteristics of the pulse, one can use methodology presented in [22]. It has been shown for hydrogen atom within numerical simulations that for short pulses, one obtains constant rate for ionization if the pulses are longer than three cycles, and hence, for such pulses, precise numerical simulations give the same results as calculations with monochromatic wave [49].

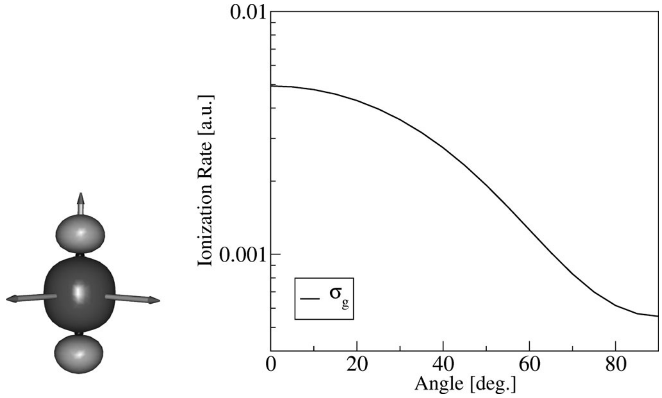

Fig. 1. (Left panel) HOMO (σ_g) isosurface for N_2. Darker gray color represents positive value of the wave function and lighter gray color negative values. (Right panel) Alignment-dependent ionization rates of HOMO (σ_g) of N_2 at a laser wavelength of 800 nm and an intensity of 5×10^{14} W · cm^{-2}.

Orientation of the molecular axis in space with respect to the polarization direction of the laser is determined in (1) via the unit vector $\hat{n}$. We are interested how the symmetry of the initial electronic wave function influences the dependence of ionization rate on the orientation angle. For all cases considered in this paper, the wave functions of the initial and final states of the neutral molecule and molecular cation, respectively, were obtained within density functional or single- and multireference correlated post-Hartree Fock methods. All results for ionization rates are shown in atomic units.

III. MOLECULES AT EQUILIBRIUM DISTANCES

One finds signatures of molecular orbital symmetry and molecular orientation in the photoelectron energy spectra and angular distributions as well as the total ionization rates and yields for laser-induced ionization of molecules. Here, we concentrate on studying only on the dependence of ionization rate on the orientation angle, namely, the angle between the axis along internuclear distance and laser field polarization direction. In this section, we present examples for the "static case," i.e., the dependence of the ionization rates on the orientation angle for diatomic molecules in their ground state at equilibrium distance. The sample of diatomics used in the analysis allows us to analyze systematically the influence of the orbital symmetry on the ionization rates since the HOMOs and inner valence shells of C_2, N_2, and O_2 belong to four classes of orbital symmetries, namely, π_u, σ_g, σ_u, and π_g. Thus, basic signatures of π versus σ, gerade versus ungerade, as well as bonding versus antibonding symmetry of an orbital can be studied qualitatively within this group of diatomics. Orientation-dependent ionization rates have been calculated by assuming a wavelength of 800 nm and laser field of intensity equal to 5×10^{14} W · cm^{-2}.

Fig. 1 presents orientation-dependent ionization rates for emission of the electron from the HOMO of N_2 along with a visualization of the HOMO (σ_g) orbital. Throughout this paper, an orientation angle of 0° corresponds to an orientation of the laser polarization along the internuclear axis of the diatomic molecule (i.e., vertical up in the visualization of the HOMO in Fig. 1). Ionization rate for N_2 attains maximum for the case when molecule is aligned along polarization direction (0°), while it is at minimum for the orientation of the polarization direction perpendicular to the molecular axis (90°). This can be intuitively understood by observing that an alignment of the molecular axis along the polarization axis corresponds to an alignment of the σ_g-orbital along the polarization direction. In a strongly linearly polarized field, the rate of ionization is expected to be maximum, if the maximum of the electronic density is aligned along the polarization direction. This expectation agrees well with the results found for the HOMO of N_2.

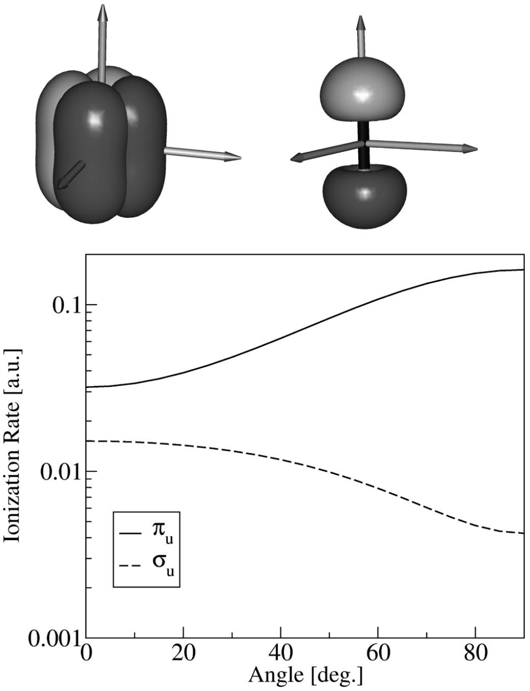

Fig. 2. (Upper panel) HOMO (π_u) and HOMO-1 (σ_u) isosurfaces for C_2. Color representation as shown in Fig. 1. (Lower panel) Comparison of alignment-dependent rates of ionization from HOMO (solid line) and inner valence orbital HOMO-1 (dashed line) of C_2. Laser parameters were the same as shown in Fig. 1.

Fig. 2 shows orientation-dependent ionization rates for HOMO (π_u, solid line) and HOMO-1 (σ_u, dashed line) orbitals of C_2. Since the π_u-orbital has a nodal plane along the internuclear axis, the ionization as a function of orientation angle has a minimum for the case when the molecule is aligned along the laser polarization direction (cf., solid line). It is more difficult to ionize the molecule when the polarization of the laser field lies in the nodal plane of the electron density. Alternatively, one can understand this result also as an interference effect of the partial electron waves arising from the parts of the wave functions with positive (darker gray color) and negative (lighter gray color) values. It is well-known from studies on atoms that the electron is preferentially emitted along the laser polarization direction. In case of a π_u-orbital with the internuclear axis aligned along the polarization direction, the interference between the partial electron waves along the polarization axis is destructive and the emission of the electron is strongly

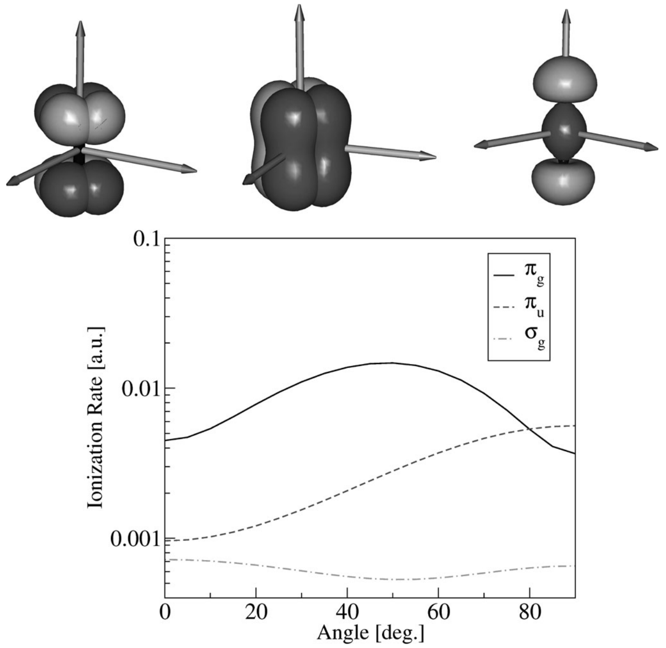

Fig. 3. (Upper panel) HOMO (π_g), HOMO-1 (π_u), and HOMO-2 (σ_g) isosurfaces for O_2. Color representation as shown in Fig. 1. (Lower panel) Orientation-dependent ionization rates for ionization, respectively, from HOMO (solid line), HOMO-1 (dotted line), and HOMO-2 (dashed line) of O_2. Laser parameters were the same as shown in Fig. 1.

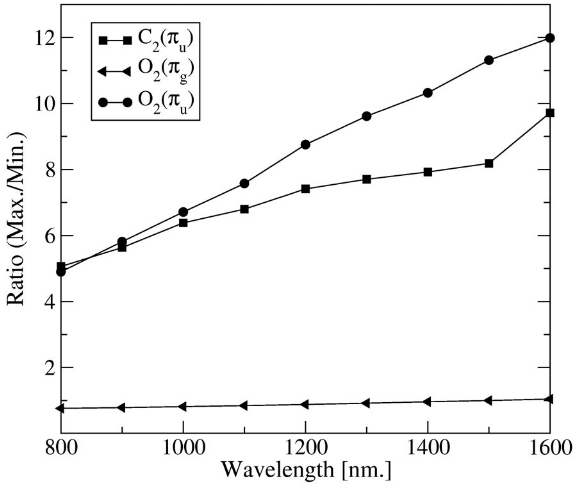

Fig. 4. Ratio of maximum to minimum for ionization rates for π-type orbitals as a function of orientation angle, shown for a range of laser wavelengths and intensity of 5×10^{14} W·cm^{-2}.

suppressed, which leads to the minimum in the total ionization rate. Analogous for orientation of the molecular π_u-orbital perpendicular to the polarization direction, the interference of the partial electron waves is constructive, and hence, the total ionization rate shows a maximum. By following the same arguments, it is easily understood that the opposite orientation dependence of ionization rate can be observed for the σ_u-orbital (cf., dashed line), where the nodal plane is perpendicular to the internuclear axis, and therefore, it is easiest to ionize the electron from this orbital when the molecular axis is aligned along the polarization direction.

Fig. 3 presents valence orbitals and orientation-angle-dependent ionization rates from orbitals for O_2. HOMO (π_g) of O_2 molecule possesses two nodal planes, and therefore, both parallel and perpendicular orientations are not favorable for ionization. Orientation dependence for ionization from HOMO-1 of π_u symmetry resembles the ionization from the same symmetry HOMO of C_2. Let us note that although usually, ionization from inner valence shells is not directly observable for strong field ionization of diatomic molecules, for O_2 for orientation angles larger than 80°, the leading contribution to ionization comes from HOMO-1 for the present laser parameters.

To sum up so far, it is seen from Figs. 2 and 3 that the alignment dependence of the ionization rate from π orbitals consistently has a minimum for 0° that is for the case when the molecular axis is parallel to the polarization direction. This is a consequence of the symmetry of the orbital, namely, that molecular orbitals of π-symmetry, like, e.g., the HOMOs of C_2 and O_2, possess a nodal plane through the body-fixed molecular axis leading to a significant reduction of ionization for this orientation. Let us note that it has been previously found that for this orientation, the same mechanism of alignment of the π-orbital nodal plane along polarization direction leads to vanishing photoelectron angular distribution along this axis, as explained in [22]. More generally, in order to maximize the orientation-dependent ionization rate in case of a π-orbital, the polarization axis has to be oriented off the nodal planes of the orbital. In contrast, in the case of HOMO for the N_2 molecule (see Fig. 1) and inner valence orbitals of C_2 and O_2 (see Figs. 2 and 3) that have σ symmetry, and thus, do not have a nodal plane along the molecular axis, the orientation-dependent ionization rate, in general, shows a maximum for 0°. Let us, however, note that the ionization rates for HOMO of N_2 and HOMO-2 of O_2 have different functional dependence on orientation angle. For N_2, the function is monotonous between angles 0° and 90° and obtains minimum for 90°, whereas for O_2, there is a minimum for some intermediate angle.

Before we proceed, we are interested in how the main features of alignment-dependent ionization rates change as a function of the wavelength of the laser. This is interesting to analyze since lasers operating at longer wavelengths in the infrared became available recently. In Fig. 4, we present the ratio of the maximum in the rate at 90° to the rate at 0° for ionization from π-orbitals as a function of the laser wavelength. Correspondingly, in Fig. 5, we present the ratio of the maximum rate at 0° to the minimum rate at 90° for the σ-orbitals. The laser intensity was chosen to be at 5×10^{14} W·cm^{-2} in all cases.

Overall, we see that the ratios, and hence, the sensitivity of the ionization rates on the alignment of the molecular orbital increase with increasing wavelength. This is expected since the strong field ionization is a highly nonlinear process. Thus, the photoelectron emission in a linearly polarized field becomes more strongly directed along the polarization direction with increasing laser wavelength, and hence, structural effects become more pronounced. In particular, the ratio is found to rise very quickly for emission from the π_u-orbital that exhibits a nodal plane along the internuclear axis.

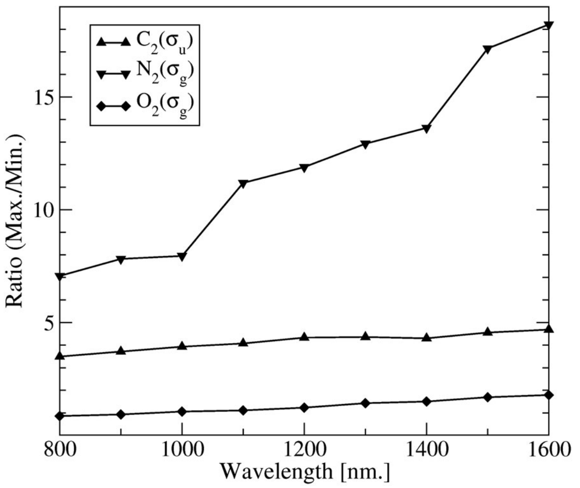

Fig. 5. Same as Fig. 4 but for σ-type orbitals.

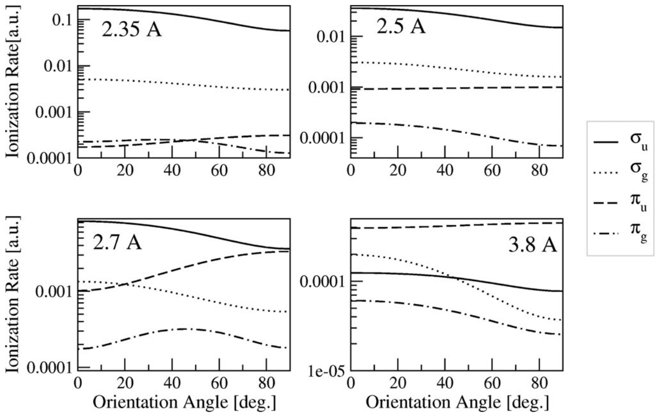

Fig. 6. Comparison of rates for ionization from all four valence orbitals of Br_2 for different internuclear distances, equilibrium distance 2.35 Å, and 2.5, 2.7, as well as 3.8 Å.

All examples analyzed in this section have been obtained by assuming that the molecule is being ionized from its ground state. However, one of the goals for strong field physics is imaging the dynamics of a system and in case of molecules, this means imaging of the electron rearrangement during chemical reactions. In the next section, we investigate such imaging prospects by using orientation-dependent ionization for dynamic electron rearrangement during the dissociation of bromine molecule. As pointed out earlier, ionization in a strong laser field is a highly nonlinear process that may enable us to image even small changes in the overall electron density as a molecule dissociates.

IV. DISSOCIATING MOLECULES

Electron dynamics plays a central role in chemical reactions. Although usually, reactions are viewed as a rearrangement of nuclear configuration, the forces acting on the nuclei are governed by the dynamics of electron rearrangement in the molecule. Therefore, with the advent of attosecond pulses that provide high intensities on ultrafast time scales, there is more and more interest in applications of ultrafast techniques to study electronic dynamics in real time. In ultrashort laser pulses, strong field ionization occurs within a few laser cycles near the peak of the pulse, and therefore, even the application of femtosecond pulses is sometimes sufficient to study electron dynamics.

To analyze this approach, we study in this section how electron rearrangement during the dissociation of bromine molecule is related to changes of the orientation-dependent ionization of the molecule. Note that our approach is valid within the Born–Oppenheimer approximation. The ground state of Br_2 has the following electronic configuration: [core]$(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(1\pi_u)^4$ $(1\pi_g)^4$ $(2\sigma_u)^0$. When the electron from the HOMO $(1\pi_g)$ is excited, e.g., to the LUMO $2\sigma_u$, the bromine molecule starts to dissociate and its dynamics as well as electron rearrangement are governed by an repulsive excited state, here, the $C(1\Pi_u)$ state. Let us note that over considerable range of internuclear distances, the configuration [core]$(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(1\pi_u)^4$ $(1\pi_g)^3$ $(2\sigma_u)^1$ is the leading electronic configuration for the molecule evolving along the $C(1\Pi_u)$ state.

We now consider ionization of the dissociating bromine molecule in its C state using a laser field with wavelength equal to 800 nm and an intensity of 4×10^{13} W·cm^{-2}. Removal of one electron from different valence orbitals in the C state of Br_2 leads to different electronic configurations of the final cation state and is related to a certain symmetry of potential energy surfaces (PESs) of the cation. For our calculations, ionization potentials for the different transitions were obtained from the difference in the PES between the C state of the neutral Br_2 and the respective PES of the cation. Note that the Br_2^+ molecular ion has a very rich structure of PES and the removal of electrons from one of the four valence orbitals $(2\sigma_g)^2$ $(1\pi_u)^4$ $(1\pi_g)^3$ $(2\sigma_u)^1$ ends in the ground or one of 29 excited states of the molecular ion.

In quantum chemical calculations, PES and corresponding wave functions were obtained by using the Gaussian basis set aug-cc-pVQZ for Hartree–Fock calculations that were followed by complete active space self-consistent field (CASSCF) calculations, and then, internally contracted multireference configuration (MRCI) calculations to include the effect of dynamical electron correlations [52], [53]. Additionally, Davidson correction [54] was applied to the MRCI energies to account for contributions from quadruple excitations. Finally, scalar relativistic corrections were included by using Douglas–Kroll–Hess approximation [55]. For the Br_2, C-state spin-orbit interactions [56] were included as well.

As noted before, within our analysis, it turns out that we have to consider possible ionization processes from the whole valence shell [$(2\sigma_g)^2$ $(1\pi_u)^4$ $(1\pi_g)^3$ $(2\sigma_u)^1$] that contributes to the total ionization rate. Fig. 6 presents the examples of orientation dependence of rates for ionization from the valence orbitals into the four energetically lowest cation states of a given symmetry (of in total 30 states) at the equilibrium distance 2.35 Å and three larger internuclear distances, namely, 2.5, 2.7, and 3.8 Å. We see that the dependence of the ionization rates on the orientation angle, in general, shows the same trends as for the basic examples in N_2, C_2, and O_2 discussed earlier. For example,

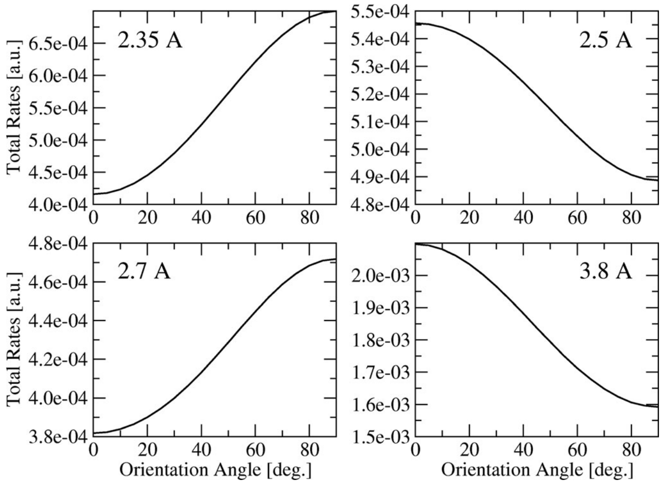

Fig. 7. Comparison of orientation-dependent rates for total ionization for different internuclear distances, equilibrium distance 2.35 Å, and 2.5, 2.7, as well as 3.8 Å.

ionization from σ-type orbitals is enhanced for the alignment of the internuclear axis along the polarization direction and is at minimum for the orientation perpendicular to the field direction. While the rates for the π_u-orbital are similar in shape to those obtained for the HOMO of C_2, those for the π_g-orbital appear to vary showing maxima at 0° or at about 45°, depending on the internuclear distance. Also, the variation of the functional dependence of the ionization rates is changing with internuclear distance.

For the actual calculations of orientation dependence of the total ionization rate, we have to consider these four contributions and those for transitions to 26 other cation states. In general, each of these contributions follow the trend analyzed earlier for a given symmetry. However, as can be seen from the comparison in Fig. 6, the relative strength of the contribution does vary with increasing internuclear distance. For example, ionization from the outermost σ_u-orbital that is the strongest among the set of four contributions at equilibrium distance is suppressed at larger internuclear distances. This variation with internuclear distance as well as the large number of possible transitions makes it difficult to *a priori* predict the dependence of the total ionization rate as a function of orientation angle at a given internuclear distance.

Indeed, for the different internuclear distances, which correspond to different times for a molecule evolving along the repulsive C state, the characteristic features of orientation dependence of the total ionization rates change significantly. We have performed calculations including all contributions for the total ionization rates and present the results in Fig. 7 for four different internuclear distances, namely, the equilibrium distance 2.35 Å, and 2.5, 2.7, as well as 3.8 Å. We see characteristic changes in the functional dependence of the total ionization rates with maxima for alignment of the molecular axis either parallel (2.5 and 3.8 Å) or perpendicular (2.35 and 2.7 Å) to the polarization direction. As mentioned earlier, in the present case, these variations reflect the electron rearrangement in the four valence orbitals of the C state of the dissociating molecule. One can see that not only HOMO contributes, but the dynamics of rearrangement is reflected in the fact that different valence orbitals are dominantly contributing to the total signal for considered internuclear distances. Note that for Fig. 7, we have chosen characteristic internuclear distances for which one can see a qualitative change in alignment-dependent ionization signal. Despite the high complexity of the analysis in the present case, including many different cation states, it is interesting to mention that a qualitative agreement between these theoretical predictions and recent experimental measurements was found [57]. This shows that observation of alignment-dependent ionization yields along with a detailed theoretical analysis may offer a powerful tool to image dynamic changes in the rearrangement of electrons in the valence orbitals of molecules, using ultrashort intense laser pulses.

V. SUMMARY

Strong field ionization of diatomic molecules as a function of orientation angle between the internuclear axis and the polarization direction of linearly polarized laser field has been studied by using the IMST. For ionization from the valence orbitals of N_2, C_2, and O_2, it is shown how the alignment-dependent ionization rates reflect the symmetry of the respective orbital. The theory has been further applied to analyze the dynamics of electron rearrangement in the four valence orbitals during the dissociation of an excited Br_2 molecule in the C state.

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